

Limits of Uncertainty of Environmental Measurements
(Using as an Example, the Dichotomous Particulate Sampler)

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LIMITS OF UNCERTAINTY OF ENVIRONMENTAL MEASUREMENTS
(Using as an Example, the Dichotomous Particulate Sampler)

by

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ABSTRACT

Two different methods are used to determine the limits of uncertainty for environmental measurements. The first, employs the general propagation of error formula. In this method, the precisions and accuracies of each of the variables of the mathematical expression defining the final measurement result are used. A second method utilizes the agreement of results from co-located samplers to estimate precision and results of independent audits to estimate bias. Each of the methods has certain advantages. The end results, using the dichotomous particulate sampler as an example, show that the use of co-located samplers reveals the presence of unaccounted for sources of error not considered by the method using the propagation of error formula.

INTRODUCTION

It is a generally-accepted axiom that decisions can be no better than the data upon which they are based. This is particularly true in the fields of environmental science, where the sources of variability are numerous and the limits of uncertainty relatively wide. Limits of uncertainty of measurement data can be determined and expressed in various ways. Such limits are generally expressed in terms of the probability or confidence limits and are arrived at from estimates of accuracy and precision of the data. The estimates of accuracy and precision can be made by two general approaches. One approach, in cases where the final environmental result is a mathematical function of a number separate measurements of various elements, involves estimating the accuracies and precisions of each of the various elements in the mathematical expression and then combining them in accordance with the rules of propagation of errors. In the second method, accuracy and precision estimates are made of the total measurement method, the accuracy being obtained from the results of blind samples submitted to the measurement procedure and the precision being obtained from the repeatability of the measurements of the same sample. For field monitoring, co-located samplers are used to accomplish repeatability. A statement of uncertainty can then be made by combining the accuracy and precision estimates. These two general approaches are illustrated by using the dichotomous sampler method for airborne particulates. For both approaches, some simplifying assumptions are made for the sake of brevity.

First, the sampling method is described. Ambient air is drawn at controlled and measured velocities into the sampler where, by airflow and particle impaction principles, the particulate is separated into two fractions, a coarse fraction with particles between 2.5 and 10 μm in aerodynamic

diameter, and a fine fraction with particles smaller than 2.5 μm . Each fraction is collected on separate Teflon filters from air drawn through the filters for a specified length of time, usually 12 or 24 hr. The filters are weighed before and after sampling to compute the particulate weight by difference. The flow rates of the air passing through each of the filters are also obtained, along with the length of time for sample collection.

To effect the correct separation of particles, the nominal flow rates and air volumes for the different air streams in the sampling system are (for a 12-hr sample --actually 705 min):

	Flow Rate L/min	Air Volume m^3
Fine	15.00	10.575
Coarse	1.67	1.177
Total	16.67	11.752

In computing the mass concentration for the fine fraction, the fine flow rate is used, and for the coarse, the total flow rate is used. (Actually, the coarse mass concentration is a function of both the coarse flow and the total flow because some fine particulates are also collected on the coarse filter.)

Method 1. Determination of Limits of Uncertainty using the Laws of Propagation of Errors

Equation 1 is a general expression for the propagation of errors. For the general function

$$\text{if } Q = f(x_1, x_2, \dots, x_n) \\ \text{then } V(Q) = \sigma_Q^2 = \sum_{i=1}^n \left(\frac{\partial Q}{\partial x_i} \right)^2 \sigma_{x_i}^2 + 2 \sum_{i,j=1, i < j}^n \left(\frac{\partial Q}{\partial x_i} \right) \left(\frac{\partial Q}{\partial x_j} \right) \rho_{x_i x_j} \sigma_{x_i} \sigma_{x_j} \quad \text{Eq. 1}$$

Under some restrictive conditions, the expression for the propagation of errors becomes simpler. If the function is strictly linear, as

$$Q = a_1 x_1 + \dots + a_r x_r + a_{r+1} x_{r+1} - \dots - a_n x_n \\ \text{where the } a_i \text{ values are numerical coefficients, then}$$

$$V(Q) = \sigma_Q^2 = \sum_{i=1}^n a_i^2 \sigma_{x_i}^2 + 2 \sum_{i,j=1, i < j}^n \rho_{x_i x_j} a_i a_j \sigma_{x_i} \sigma_{x_j} \quad \text{Eq. 2}$$

where $\rho_{x_i x_j}$ is the correlation coefficient between the errors.

Equation 2 is called by some the "Variance of a Linear Function" and has many valuable applications. This general formula reduces to simpler expressions to handle the two basically different functions, namely additive and multiplicative. For the additive function when there are no correlations among the errors, the second term of Equation 2 is dropped leaving simply

$$V(Q) = \sum a_i^2 \sigma_{x_i}^2 \quad \text{Eq. 3}$$

And for the multiplicative function:

$$\begin{aligned} \text{if } Q &= a \left(\frac{x_1 x_2 \dots x_r}{x_{r+1} \dots x_n} \right) \\ \text{then } \left(\frac{\sigma_Q}{Q} \right)^2 &= \sum_{i=1}^n \left(\frac{\sigma_{x_i}}{x_i} \right)^2 \end{aligned}$$

Since $(\sigma_Q/Q)^2$ and $(\sigma_{x_i}/x_i)^2$ are the respective squares of the coefficients of variation (CV), the above can be written in simpler terms as

$$CV^2(Q) = \sum_{i=1}^n C V_{x_i}^2 \quad \text{Eq. 4}$$

For complex expressions involving both additive and multiplicative functions it is often simpler to apply Equations 3 and 4, in successive steps for selected portions of the expression until the complete complex expression is considered, rather than use the very general formula, Equation 1, for propagation of errors. This stepwise procedure cannot be used, however, when the same variable is repeated in different steps, or when there are correlated variables across steps. Both procedures are used below for the fine particulate concentration from the dichotomous sampler to demonstrate their equivalency. (Computations are carried out to more decimals than normally needed to demonstrate exact equivalency of the two different procedures, and final results are rounded off.) But first some relationships are developed which are needed for later computation.

The functional relationship for the concentration of fine particulate is

$$[F] = (w_e - w_u)/Qt$$

where [F] = fine concentration, $\mu\text{g}/\text{m}^3$
 w_e = weight of the exposed filter, μg
 w_u = weight of the unexposed filter, μg
 Q = flow rate, m^3/min
 t = sampling time, min

In this simple example, the numerator, N, can be handled according to the additive Equation 3; the denominator, D, according to the multiplicative Equation 4; and finally the fraction, N/D, according to the multiplicative Equation 4. In doing this, care must be taken to convert from standard deviations (for the additive rule) to coefficients of variation (for the multiplicative rule), or vice versa, whenever changes are made between uses of the two rules.

In a recent study, the standard deviations, s, of the differences between duplicate weighings of the unexposed and exposed filters were 0.008 mg and 0.010 mg, respectively. Because the differences involve two independent

weighings, the standard deviations of weighing errors for individual filters are $0.008/\sqrt{2} = 0.0057$ and $0.010/\sqrt{2} = 0.0071$ for unexposed and exposed filters, respectively. This follows, since if $D = W_1 - W_2$

where: D = difference therefore: $s_D^2 = s_{W_1}^2 + s_{W_2}^2 = 2s_W^2$ *

W_1 = first weight

W_2 = second weight and $s_D = \sqrt{2} s_W$

The particulate weight, W , for either coarse or fine fractions, is the difference in the weights of the exposed and unexposed filters

where: $W = w_e - w_u$ therefore: $s_W^2 = s_{w_e}^2 + s_{w_u}^2$ *

w_e = exposed weight

w_u = unexposed weight and $s_W = \sqrt{0.0071^2 + 0.0057^2}$
= 0.0091 mg

The 95% confidence limits, or 95% limits of uncertainty for a particulate weight, coarse or fine, is

$$\pm 1.96(0.0091) \quad \text{or} \quad \pm 0.0182 \text{ mg}$$

The simplified expression for total particulate weight is $W_T = W_c + W_f$

where: W_T = total particulate weight

W_c = coarse particulate weight

W_f = fine particulate weight

therefore: $s_{W_T}^2 = s_{W_c}^2 + s_{W_f}^2$ *

$$s_{W_T} = \sqrt{0.0091^2 + 0.0091^2} = 0.0129 \text{ mg}$$

The 95% limits of uncertainty for the total particulate weight is therefore:

$$\pm 1.96(0.0129) \quad \text{or} \quad \pm 0.0258 \text{ mg}$$

Note: This variability is considered the same regardless of the amount of particulate involved. (This assumption needs to be verified.) The following values indicate the values of the coefficients of variation at various particulate weights.

Weight, mg	Coefficient of Variation
0.1	$0.0129/0.1 = 13.0\%$
0.5	$0.0129/0.5 = 2.6\%$
1.0	$0.0129/1.0 = 1.3\%$
2.0	$0.0129/2.0 = 0.65\%$

* Note that each of the asterisked expressions above is a simple application of the Variance of a Linear Function, Equation 2.

From separate studies, it has been determined that the coefficient of variation for flow rate measurement is 3.0%, or

for Coarse: 0.03(1.67) = 0.050 L/min
 Fine: 0.03(15.0) = 0.450 L/min
 Total: 0.03(16.67) = 0.500 L/min

For the sampling time, t , it is reasonable to believe that errors in recording time would be no larger than ± 5 min. Assuming these limits to correspond to ± 2 standard deviations, the standard deviation is 2.5 min, corresponding to a coefficient of variation of 0.355% for a sampling time of 705 min.

Limits of Uncertainty for Fine Concentration

Stepwise Procedure. Computation of limits of uncertainty for the fine concentration, $[F]$, at 50 $\mu\text{g}/\text{m}^3$, is shown below using the stepwise procedure. The necessary input data are

$s_e - s_u = 528.75 \mu\text{g}$	$s_e = 0.0071 \text{ mg} = 7.1 \mu\text{g}$	
	$s_u = 0.0057 \text{ mg} = 5.7 \mu\text{g}$	
$Q = 0.015 \text{ m}^3/\text{min}$	$s_Q = 0.450 \text{ L/min}$	$CV_Q = 3.0\%$
	$= 0.00045 \text{ m}^3/\text{min}$	
$t = 705 \text{ min}$	$s_t = 2.5 \text{ min}$	$CV_t = 0.355\%$

$$[F] = (w_e - w_u)/Qt = N/D$$

In all of the computations that follow, using Equations 3 and 4, sample standard deviations, s , are used as estimates of σ , sample correlation coefficients, r , will be used as estimates of ρ , and sample coefficients of variation, CV , are used. Note that no separate allowances are made herein for the limited degrees of freedom of the estimates of the measurement error variation. Such considerations could be introduced with more complexity of the computations.

By using the additive Equation 3 for the numerator, N ,

$$\begin{aligned} s^2(N) &= s_{w_e}^2 + s_{w_u}^2 \\ &= 7.1^2 + 5.7^2 \\ &= 82.90 \\ s(N) &= 9.105 \mu\text{g} \\ CV(N) &= \frac{9.105}{528.75} = 1.722\% \end{aligned}$$

By using the multiplicative Equation 4 for the denominator, D ,

$$\begin{aligned} CV^2(D) &= CV^2(Q) + CV^2(t) \\ &= 3.0^2 + 0.355^2 \\ &= 9.1260 \\ CV(D) &= 3.021\% \\ s(D) &= 3.021\%(0.015)(705) = 0.3195 \text{ m}^3 \end{aligned}$$

Then, by using the multiplicative Equation 4 for the fraction, N/D ,

$$\begin{aligned}
 CV^2[F] &= CV^2(N) + CV^2(D) \\
 &= 1.722^2 + 3.021^2 \\
 &= 12.092\%
 \end{aligned}$$

Observe that the contribution of the numerator is small.

$$s[F] = 3.477\%(50) = 1.739 \mu\text{g}/\text{m}^3$$

The 95% limits of uncertainty are therefore

$$\begin{aligned}
 &50 \pm 1.96(1.739) \\
 &\text{or } 46.592 \text{ and } 53.408 \mu\text{g}/\text{m}^3
 \end{aligned}$$

General Formula. For comparison, and to show the exact equivalency of the general formula for propagation of error, Equation 1, for the fine particulate concentration at $50 \mu\text{g}/\text{m}^3$:

$$\begin{aligned}
 [F] &= \frac{w_e - w_u}{Qt} & \text{Eq. 5} \\
 \sigma^2[F] &= \left(\frac{\partial F}{\partial w_e}\right)^2 \sigma_{w_e}^2 + \left(\frac{\partial F}{\partial w_u}\right)^2 \sigma_{w_u}^2 + \left(\frac{\partial F}{\partial Q}\right)^2 \sigma_Q^2 + \left(\frac{\partial F}{\partial t}\right)^2 \sigma_t^2 \\
 &= \left(\frac{1}{Q_t}\right)^2 (7.1)^2 + \left(\frac{-1}{Qt}\right)^2 (5.7)^2 + \left(\frac{-(w_e - w_u)}{tQ^2}\right)^2 (0.00045)^2 + \left(\frac{-(w_e - w_u)}{Qt^2}\right)^2 (2.5)^2 \\
 &= \left(\frac{1}{(.015)(705)}\right)^2 (7.1)^2 + \left(\frac{-1}{(.015)(705)}\right)^2 (5.7)^2 + \left(\frac{-(528.75)}{(705)(.015)^2}\right)^2 (.00045)^2 \\
 &\quad + \left(\frac{-(528.75)}{(.015)(705)^2}\right)^2 (2.5)^2 \\
 &= \frac{w_e^2}{Q^2} + \frac{w_u^2}{Q^2} + \frac{Q^2}{t^2} + \frac{t^2}{Q^2} \\
 &= .45077 + .29053 + 2.25000 + .03144 \\
 &= 3.02274 \quad (14.9\%) \quad (9.6\%) \quad (74.4\%) \quad (1.0\%)
 \end{aligned}$$

$$s[F] = 1.73860 \mu\text{g}/\text{m}^3$$

Therefore, the 95% limits of uncertainty are exactly the same as previously computed by Equations 3 and 4.

$$50 \pm 1.96 (1.7380) \text{ or } 46.592 \text{ and } 53.408 \mu\text{g}/\text{m}^3$$

Note that the percentage values in parentheses above are the relative contributions of the errors of exposed weight, unexposed weight, flow rate, and time, respectively. These percentages clearly show the predominance of the flow rate errors. This procedure thus provides the advantage of revealing the relative contributions to the total error which are further represented by the use of successive right triangles shown in Figure 1. In Figure 1, the lengths of Q_t , w_e , w_u , and t represent the individual contributions made by the variances of these variables to the variance of $[F]$. It is clear from the successive application of the Pythagorean Theorem that

$$Q_t^2 + w_e^2 + w_u^2 + t^2 = [F]^2$$

where Q_t really represents $(\partial Q_t / \partial [F]) \sigma_{Q_t}$, and similarly for the other variables.

Limits of Uncertainty of the Coarse Concentration

Computation for the coarse concentration is somewhat more complicated since it also involves the fine concentration according to the following equation:

$$[C] = ((w_e - w_u) - [F]Q_c t) / Q_t t$$

where Q_c = coarse flow rate
 Q_t = total flow rate

After performing the detailed computations to determine the limits of uncertainty for $[C]$, at $[F] = 50 \mu\text{g}/\text{m}^3$ and $[C] = 25 \mu\text{g}/\text{m}^3$, the results are

$$s^2[C] = \frac{w_e}{(29.8\%)} + \frac{w_u}{(19.2\%)} + \frac{[F]}{(2.5\%)} + \frac{Q_c}{(1.8\%)} + \frac{Q_t}{(45.8\%)} + \frac{t}{(0.9\%)}$$

$$s^2[C] = 1.22664$$

$$s[C] = 1.108 \mu\text{g}/\text{m}^3$$

The 95% limits of uncertainty are therefore

$$25 \pm 1.96(1.108) \text{ or } 22.8 \text{ and } 27.2 \mu\text{g}/\text{m}^3$$

The percentage contributions show that the total flow rate is the greatest contributor (45.8%) to variability of the coarse concentration. And this does not consider any separate effect on the actual separation of coarse and fine particles, which would be an added effect. The graphical representation of the relative contributions are shown in Figure 2.

Limits of Uncertainty of the Total Concentration

A similar graphical representation of the relative contributions to the total particulate concentration is shown in Figure 3, showing the following percentage contributions:

Flow Rates	67.2%
Fine	53.5%
Coarse	0.5%
Total	13.2%
Filter Weights	31.7%
Exposed	19.3%
Unexposed	12.4%
Sampling Time	1.0% 1.0%

Additional computations were completed to show the standard deviation and coefficients of variation for $[F]$ and $[C]$ at various concentration levels and coarse/fine ratios (Figures 4 and 5). The 2-sigma values for limits of uncertainty for total particulate are shown in Figure 6 for various combinations of $[F]$ and $[C]$. For example, if the $[F]$ is $80 \mu\text{g}/\text{m}^3$ and the $[C]$ is $50 \mu\text{g}/\text{m}^3$, the 2-sigma value as read from the Figure 6 is $8.6 \mu\text{g}/\text{m}^3$. The 95% limits of uncertainty for the total particulate concentration are

$$130 \pm (8.6) \text{ or } 121.4 \text{ and } 138.6 \mu\text{g}/\text{m}^3$$

All of the preceding computations assume that there are no correlations among the errors. If the coefficients of the correlated variables in the original equation are of the same sign, positive correlations of the errors will increase the total error, and negative correlations of the errors will decrease the total error. However, if the coefficients of the correlated variables in the original equation are of opposite signs, positive correlations of the errors will decrease the total error and negative correlations will increase the total error. A discussion of known or very likely correlations follows.

Because the time of sampling is identical for both coarse and fine concentrations, the two times are exactly the same and thus are positively correlated with a coefficient of 1.00. There is also reason to believe that the errors of weighing and flow rate are also positively correlated since these measurement systems are calibrated at the same time and measured in the field at the same time. However, the correlations of errors among the flow rates would depend upon how the flow rates are calibrated and measured. If all the flow rates are determined separately, they could all be correlated in a positive way. However, as has been the practice in the past, the total and coarse flows are calibrated separately and the fine flow is obtained by difference. In this case, the fine flow would be positively correlated with the total, but negatively correlated with the coarse flow rate.

The weighing errors are more than likely positively correlated since the weighing balance used is the same for both fine and coarse filters and thus have a common error. The other errors in weighing such as those due to conditioning are more than likely to be positively correlated since the unexposed filters for fine and coarse fractions are weighed at nearly the same time and likewise for the exposed filters. The effects of conditioning on the weighing errors may be different for the exposed and unexposed filters since they are weighed at different times. There is no reason to believe that the errors of time and weighing, or flow rate and weighing are correlated.

Computations based on the [F]=50, [C]=25 case show that considering the coarse flow and total flow are negatively correlated with a coefficient of -1.00, this effect becomes the largest single contributor and increases the total variance of [C] by 17% and the standard deviation by 8%. Accordingly, the limits of uncertainty for [C] would be increased by $\pm 8\%$. The 95% limits of uncertainty would be

$$25 \pm 1.96(1.20) \text{ or } 22.6 \text{ and } 27.8 \mu\text{g}/\text{m}^3$$

If the worst likely correlations are assumed for the following variable pairs

<u>Variable Pair</u>	<u>Correlation Coefficient</u>
coarse and fine sampling times	1.00
coarse and fine exposed weights	1.00
coarse and fine unexposed weights	1.00
total and fine flow rates	1.00
coarse and fine flow rates	1.00
total and coarse flow rates	-1.00

computations show a 100.6% increase in the variance and a 41.6% increase in the standard deviation for the total particulate concentration at [F] = 50 and [C] = 25 $\mu\text{g}/\text{m}^3$. The 95% limits of uncertainty become

$$75 \pm 5.7 \text{ or } 69.3 \text{ and } 80.7 \mu\text{g}/\text{m}^3$$

No consideration of biases have been made in the above computations. The treatment of biases under Method 1 would be the same as that considered below under Method 2.

Method 2. Uncertainty Limits Based on Accuracy and Precision of the Method

Precision of the total method can be estimated from the agreement of results from co-located samplers. Suppose that the paired data from a large number of samplings from a pair of co-located samplers resulted in the following differences:

	<u>Signed Differences ($\mu\text{g}/\text{m}^3$)</u>	
	<u>Average</u>	<u>Standard Deviation</u>
Coarse	1.50	3.27
Fine	.66	2.65
Total	1.08	2.98

For the moment, assume that the average differences are not significantly different from zero. Thus, there is not a significant bias between the two samplers. The estimate of uncertainty then is a function only of the variability or standard deviation of the differences. The standard deviation for a single value for a coarse mass value is $3.27/\sqrt{2}$, or 2.31, and for the fine mass value, $2.65/\sqrt{2}$, or 1.87.

Considering only these precision estimates, the 95 % probability limits for uncertainty of single reported values are

$$\pm 1.96(2.31), \text{ or } \pm 4.53 \mu\text{g}/\text{m}^3 \text{ for coarse} \\ \text{and } \pm 1.96(1.87), \text{ or } \pm 3.67 \mu\text{g}/\text{m}^3 \text{ for fine.}$$

And if the errors in the coarse and fine measurements are completely independent and uncorrelated, then the 95 percent limits of uncertainty for the total particulate would be

$$\pm 1.96\sqrt{2.31^2 + 1.87^2} = \pm 1.96(2.97) \\ \text{or } \pm 5.83 \mu\text{g}/\text{m}^3$$

The above values were obtained during sampling when the coarse values varied between 0.4 and 26.9 $\mu\text{g}/\text{m}^3$, with an average of 8.4, and the fine values varied between 8 and 54 $\mu\text{g}/\text{m}^3$, with an average of 19.0.

Considerations for Accuracy or Bias. Unfortunately, there is no practical way to estimate the accuracy for the entire method. However, separate accuracy estimates can be made of the weighing, the flow measurements, and the time of sampling. For simplicity, however, let us assume that the errors of accuracy for weighing and time are negligible and that the main source of bias error is the flow measurements.

Suppose that the independent audits of the flow rates from a large number of audits were reported as follows:

<u>Signed Differences (L/min)</u> <u>(Observed - Audit Value)</u>	<u>Coarse</u>	<u>Fine</u>	<u>Total</u>
Average	0.055	-0.154	0.143
Standard Deviation	0.043	0.612	0.524

The equivalent values in terms of $\mu\text{g}/\text{m}^3$ are:

Average	0.065	-1.629	1.684
Standard Deviation	0.051	6.472	6.170

Now, suppose that the standard deviations are negligible, even though they are not, and suppose that the average values of the signed differences are significantly different from zero, thereby representing estimates of the bias of the flow rates used in computing concentrations. The bias can be combined with the precision in two different ways to compute limits of uncertainty depending upon the assumptions one can make concerning the particular measurement system, the particular data set involved, how the estimates of bias were obtained, and the use to which the limits are to be put. (There is no universal agreement as to which procedure is more appropriate.) If the bias is believed to be very persistent and has been determined from a large number of values, and is to be used only for a limited data set from which bias is estimated, then the bias should be added directly to (actually subtracted from) the limits based on precision to produce asymmetric limits, as

$$\pm 1.96(\text{precision}) - (\text{bias}) \quad \text{Eq. 6}$$

However, if the bias has been estimated from a limited number of audits and therefore not exactly determined, if the bias may be considered itself as a variable from time to time, and if the limits are to be generally applied to the measurement method, then the bias should be added in quadrature, as

$$\pm 1.96\sqrt{(\text{precision})^2 + (\text{bias})^2} \quad \text{Eq. 7}$$

In either case, the above uncertainty limits should not be considered as 95 % probability or confidence limits in the strict statistical sense, because the bias is, by definition, not random. Some authorities use the expression -- "uncertainty limits with 95 % coverage".

Similar considerations must be made when several biases are combined for the same total measurement system, such as biases for flow rate, weighing, and time measurements.

If the estimates of precision and flow rate bias given above are used, the limits of uncertainty for 95 % coverage about an observed value become--

for Coarse, adding bias directly

$$\pm 1.96(2.31) - 1.684$$

$$-6.21 \text{ and } + 2.84 \mu\text{g}/\text{m}^3 \text{ with a spread of } 9.05$$

for Coarse, adding bias in quadrature

$$\pm 1.96 \sqrt{2.31^2 + 1.684^2}$$

$$\pm 4.82 \mu\text{g}/\text{m}^3 \text{ with a spread of } 9.64$$

for Fine, adding bias directly

$$\pm 1.96(1.87) - (-1.629)$$

$$- 2.04 \text{ and } + 5.29 \mu\text{g}/\text{m}^3 \text{ with a spread of } 7.33$$

for Fine, adding bias in quadrature

$$\pm 1.96 \sqrt{1.87^2 + 1.629^2}$$

$$\pm 4.86 \mu\text{g}/\text{m}^3 \text{ with a spread of } 9.73$$

for Total, adding the bias directly

$$\pm 1.96(2.97) - 1.684$$

$$-7.51 \text{ and } + 4.14 \mu\text{g}/\text{m}^3 \text{ with a spread of } 11.65$$

for Total, adding the bias in quadrature

$$\pm 1.96 \sqrt{2.97^2 + 1.684^2}$$

$$\pm 6.69 \mu\text{g}/\text{m}^3 \text{ with a spread of } 13.38$$

The above uncertainty limits apply only to the particular data set involved since they are not computed as a function of concentration level.

Limits of uncertainty for the Total particulate concentration can be determined in a slightly different way by combining the precisions and biases of the coarse and fine, as

for Total, combining the precisions and adding the biases directly

$$\pm 1.96(2.97) - 1.684 - (-1.629)$$

$$-5.88 \text{ and } + 5.77 \text{ } \mu\text{g}/\text{m}^3 \text{ with a spread of } 11.64$$

for Total, combining the precisions and biases in quadrature

$$\pm 1.96 \sqrt{2.31^2 + 1.87^2 + 1.684^2 + 1.629^2}$$

$$\pm 7.42 \text{ } \mu\text{g}/\text{m}^3 \text{ with a spread of } 14.84$$

The above values for total particulate concentration are in fair agreement whichever way the limits are calculated.

Comparison of Methods 1 and 2. A comparison of the two methods can be made only at the same concentration levels, namely those occurring for the co-located samplers used for Method 2, when the average value for [C] was $8.4 \mu\text{g}/\text{m}^3$ and for [F], $19.0 \mu\text{g}/\text{m}^3$. Using Method 1 and assuming the worst likely correlations as listed on page 9, and at [C] = $8.4 \mu\text{g}/\text{m}^3$ and [F] = $19.0 \mu\text{g}/\text{m}^3$, the 95% limits of uncertainty for [T] are 27.4 ± 3.72 , or 23.7 and $31.1 \mu\text{g}/\text{m}^3$. The following table summarizes the comparisons at these concentration levels.

Width of 95% Limits of Uncertainty for [T]
at [C] = 8.4 and [F] = $19.0 \mu\text{g}/\text{m}^3$

Considering--	Method 1 Propagation of Error Formula	Method 2 Co-located Samplers and Performance Audits
Precision Only	± 2.64	
Precision Plus Worst Likely	± 3.72	± 5.83 (The effects of any correlations are built into the co-located results)
Precision Plus Bias of Flow Rates		± 6.69 ± 7.42

Since the limits are 60% wider for Method 2 than for those using the propagation of error formula (Method 1) even with the worst likely correlations, there evidently are other sources of variability in the real world that are not considered by the formula. Some of these other sources could be--

1. variation in flow rates during the sampling period and their separate effects on particle separation.
2. drifts in the weighing measurement system.
3. losses of particulate during handling prior to final weighing.

4. losses of filter fibers during sampling, sample handling, and prior to the final weighing.
5. variation in the effects of filter conditioning prior to weighing.

Therefore, the most realistic limits are those obtained from co-located samplers with additional considerations for biases obtained from performance audits.

CONCLUSIONS

The relative and absolute effects of different variables on limits of uncertainty for coarse, fine, and total particulate concentrations have been computed through the propagation of error analysis and graphically presented. At low concentrations, the errors of weighing predominate the effects, and at higher levels, the errors of flow rate predominate. Errors in the sampling time have very little effect. A second method using the agreement of results from co-located samplers to estimate precision of the total method and results of performance audits to estimate accuracy or bias, reveals that some sources of variability are not accounted for by the use of the propagation of error formula.

RECOMMENDATIONS

Accuracy and precision data for the various measurement systems should be used more effectively in the determination of limits of uncertainty of air monitoring data. More analyses should be performed to determine the relative contributions to variation, to indicate more quantitatively the importance of errors of particular variables. Further efforts should be made to reduce the error variation of the predominant variables because this will yield the greatest benefit in reducing the limits of uncertainty of the pollutant concentrations.

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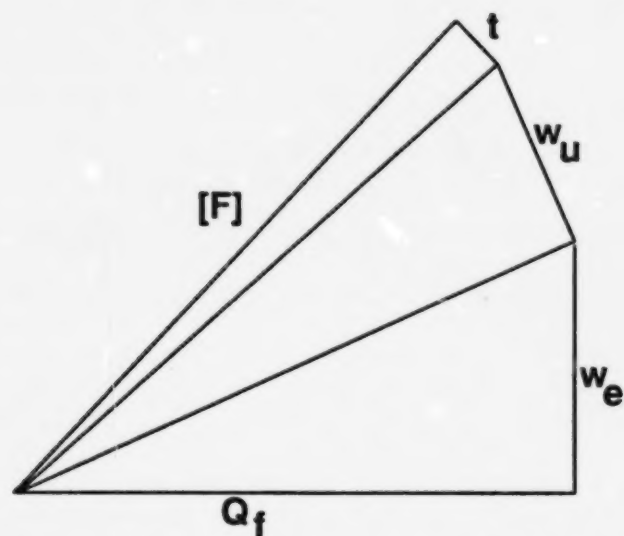


Figure 1. Relative contributions to measurement error of fine particulate concentration at $[F] = 50 \mu\text{g}/\text{m}^3$

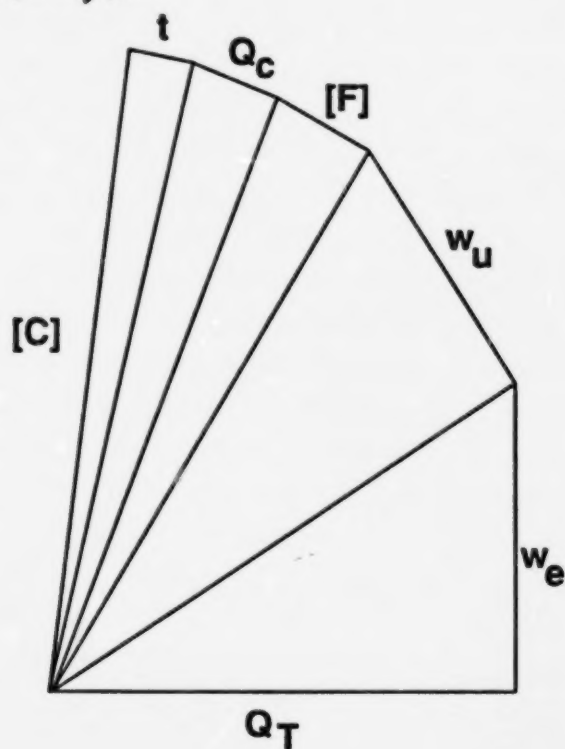


Figure 2. Relative contributions to measurement error of coarse particulate concentration at $[C] = 25 \mu\text{g}/\text{m}^3$ and $[F] = 50 \mu\text{g}/\text{m}^3$.

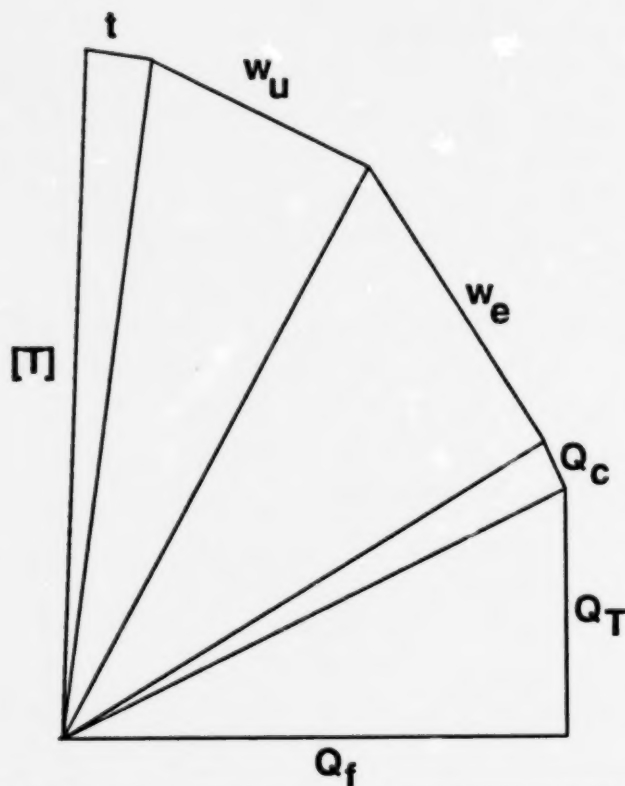


Figure 3a. Relative contributions to measurement error of total particulate concentration at $[C] = 25 \mu\text{g}/\text{m}^3$ and $[F] = 50 \mu\text{g}/\text{m}^3$.

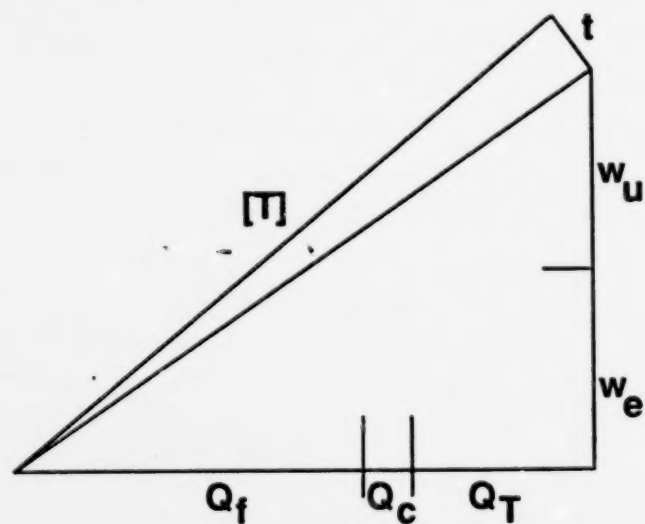


Figure 3b. Relative contributions to measurement error of total particulate concentration at $[C] = 25 \mu\text{g}/\text{m}^3$ and $[F] = 50 \mu\text{g}/\text{m}^3$.

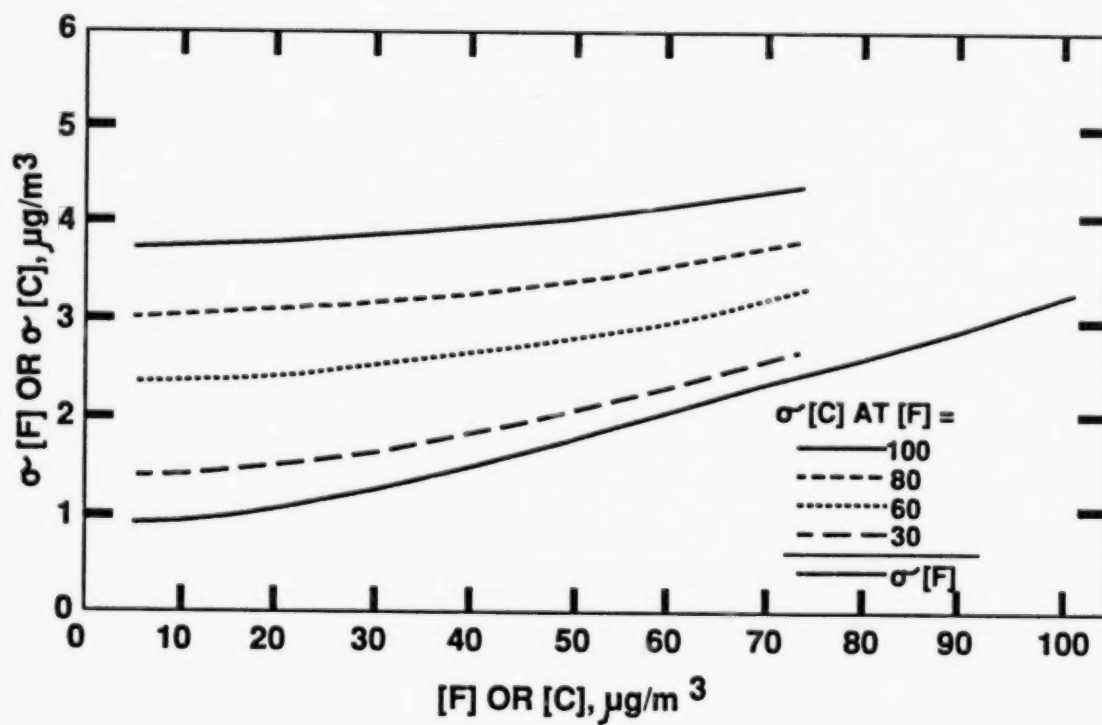


Figure 4. Standard deviation of coarse and fine particulate contributions.

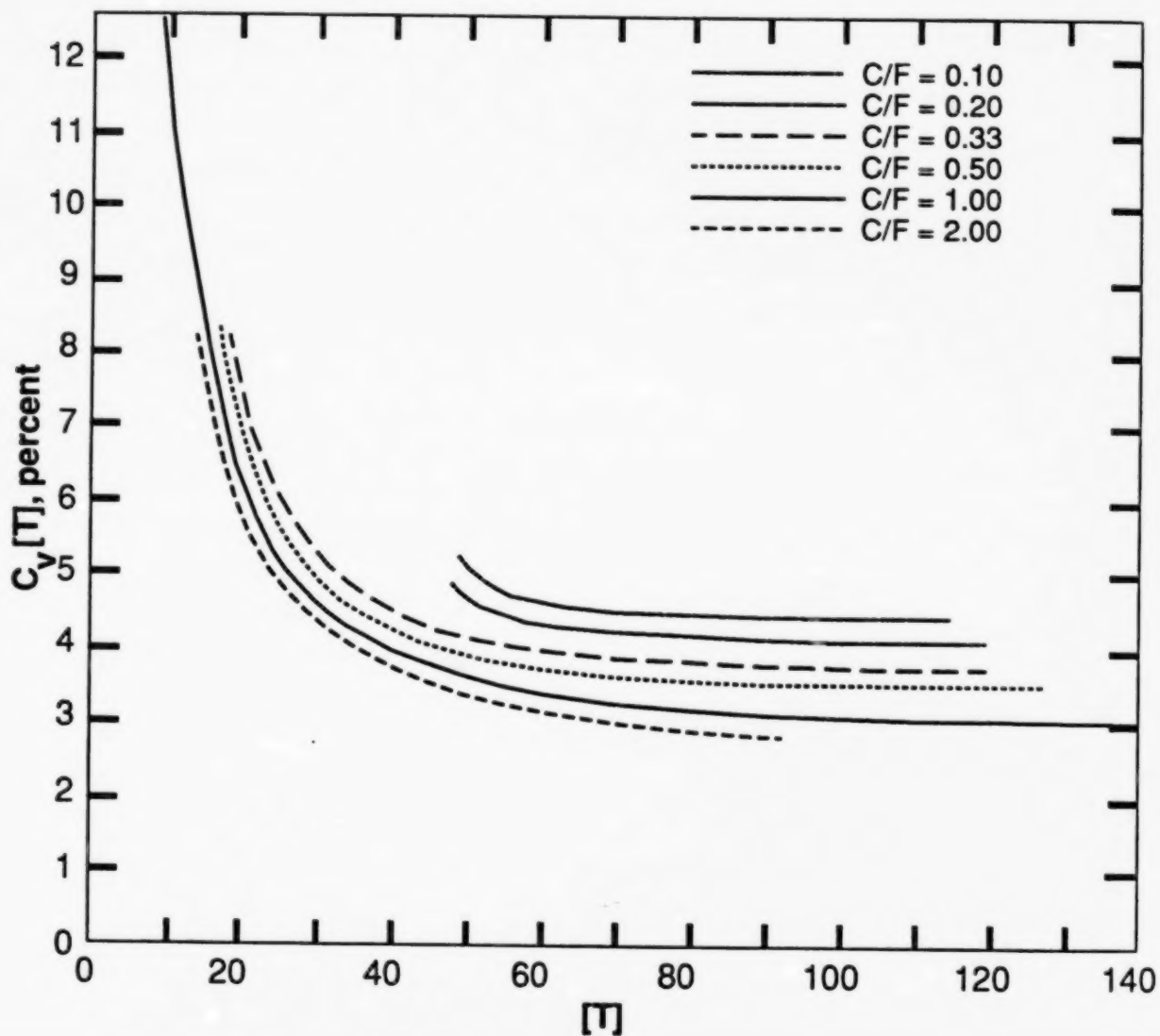


Figure 5. Coefficient of variation of measurement errors for total particulate concentration.

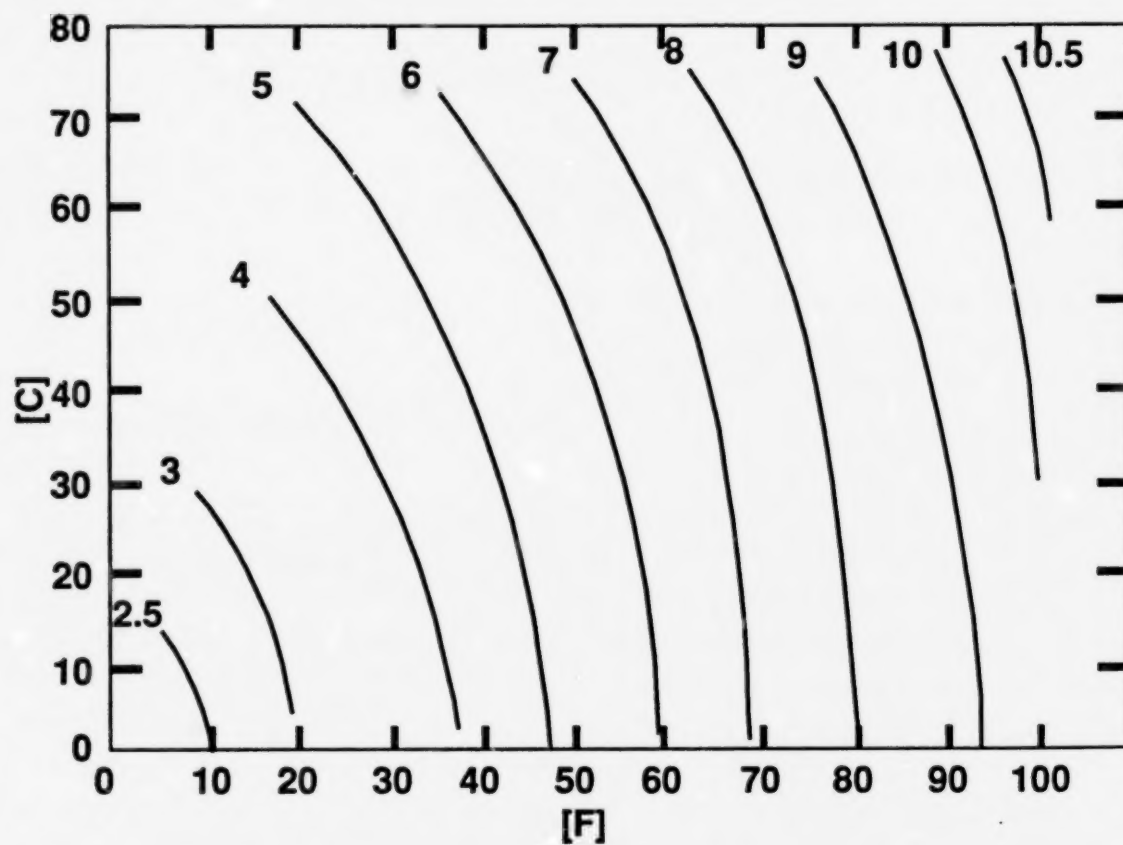


Figure 6. Two-sigma values for measurement errors of total particulate concentration, in $\mu\text{g}/\text{m}^3$, as a function of coarse and fine concentrations.